*Proceedings of the 1st International Conference on Natural Resources Engineering & Technology 2006*
*24-25th July 2006; Putrajaya, Malaysia, 243-254*

# Hydrocracking of Gas Oil using USY-Zeolite-Based Catalyst

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**Abstract**

The conversion of petroleum gas oil to transportation fuels was investigated using NiMo, CoMo, NiW and CoW catalysts supported on commercial USY zeolite. The catalysts were prepared using the incipient wetness method. The reaction was carried out in a high-pressure shaking reactor at reaction temperature of 450 $^{o}$C, contact time of 90 minutes and catalyst to sample ratio of 0.04. It was found that over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 64.35 and 54.12 wt%, respectively, compared to 46.48 and 38.25 wt% over unloaded USY zeolite. The hydrocracking activities of other USY-based catalysts were increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. The catalysts were characterized by TGA-TPD acidity, TGA thermal stability, and BET surface-area measurements.

*Keywords: Petroleum gas oil, USY-based catalyst, high-pressure shaking reactor.*

## 1.0 Introduction

The global demand for crude oil has increased by 150 % over the last 40 years and 20 % in the past two decades to the current 80 million barrels per day and is projected to grow by 50 % more in the next 20 years [1]. The demand for lighter products (LPG, gasoline) and middle distillates (jet fuels, diesel) has grown steadily as a result of transportation demand, and the majority of machines and equipments being made at present are designed to run using liquid fuel. In petroleum refining, hydrocracking of heavy hydrocarbons has been carried out to produce high quality gasoline, jet fuel and diesel. Hydrocracking process needs dual function catalysts, hydrogenation and cracking functions. Active component and promoters sulphides provide hydrogenation function, while supports provide the cracking functions. Active components are commonly transition metal sulphides of an element in group VIB (i.e. molybdenum (Mo) or tungsten (W)) that responsible for the principal chemical reaction. The active components saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalyst from poisoning by the coke. A promoter is a chemical compound such as nickel (Ni) and cobalt (Co) which when added results in desirable activity, selectivity or stability effects. With addition of the promoter, the strength of Lewis sites and the number of Bronsted sites are increased, and the enhancement in catalytic activity is significant [2]. The role of the promoter is to increase the number of sulphur vacancies and to modify the acid-base properties of the catalyst. The presence of promoter also enhances the liability of sulphur anions, thus leading to more numerous of active sites in the reductive atmospheric of the hydrotreating processes.

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Mijoin [3] and Breysse et al. [4] concluded that the activity of the promoter catalysts for debenzothiophene transformation is 20 times higher than the activity of the non-promoter catalyst The use of Co or Ni carbonyls as a precursor was reportedly effective to a preferential formation of Co(Ni)MoS phase [5].

Supports provide the cracking functions, where the cracking takes place on strong acid sites in the supports. The most important function of support is maintenance of high surface area for the active component and acidity for hydrocracking reactions. A support material is chosen for given application on the basis of the several important characteristics including its inertness to undesired side reactions, appropriate mechanical properties (attrition resistance, strength, etc), stability under reaction conditions, a surface area and pore size distribution appropriate for the desired reaction, and its cost [6]. Zeolites are widely used as catalyst support and play an important role in the catalysts used in hydrocracking process because they improve catalytic activity, selectivity, or stability by imparting shape selectivity [7]. Zeolites are defined as crystalline aluminosilicates, have been investigated and extensively used in industry. Zeolites have been successful because of their crystallinity, high surface area, adsorption capacity, and uniform size distribution which enable shape selectivity. The elementary building units of zeolites are $SiO_4$ and $AlO_4$ tetrahedra. Among the properties which are affected by the framework alumina content are the density of negative framework charges, cation-exchange capacity, the density of Bronsted acid sites, their strength and thermal stability [8]. For the majority of catalytic applications, medium or large pore zeolites will usually be preferred. In the processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates, the catalytic activity stems from the Bronsted acid sites rather than the Lewis acid sites. It is well known, due to the higher electronegativity of silicon compared to alumina, the strongest Bronsted acid sites in zeolites will occur on completely isolated $AlO_4$-tetrahedra. This is the reason why, upon dealumination of Y-zeolites with typical Si/Al ratio of 2.5, the catalytic activity generally increase up to Si/Al ratio of 10. In this region, the gain in acid strength overcompensate the decrease in the density of Bronsted acid sites [8].

Many catalysts used for the hydrocracking process are formed by composting various transition metals with the catalyst supports such as alumina, silica, alumina-silica, magnesia, and zeolites [9-16]. High activity levels can be achieved with zeolites, which is not the case with conventional silica–alumina. The reason of the high activity and cracking selectivity of zeolites is their strong acidity which favours successive cracking reactions, and as a consequence, the formation of light products. It is an interesting line of research to use USY zeolite as catalyst support because it is play an important role in the catalysts used in hydrocracking process and there is lack in using it for hydrocracking of heavy oil. Sato et al. [17] carried out the hydrocracking of tetralin over NiW/USY zeolite catalysts using a 50 ml batch reactor. Their results revealed that hydrocracking over NiW/USY is superior to that over USY only in the longer reactions. This difference is due to the limited role of NiW sulphide in the hydrocracking of tetralin. NiW sulphide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over acid sites. The conversion over USY was almost the same as that over NiW/USY for the first 10 min and slightly lower in a longer reaction. Hassan et al. [18] compared between β and USY zeolite-based hydrocracking catalysts for hydrotreated vacuum gas oil (HT-VGO) using two series: $\gamma$-$Al_2O_3$ and β-zeolite ($SiO_4$/ $Al_2O_3$ molar ratio =24) in the first series and $\gamma$-$Al_2O_3$ and USY-zeolite ($SiO_4$/ $Al_2O_3$ =6) in the second series. Nickel and tungsten were loaded as active metals on these supports. They reported that β-zeolite-based catalysts showed higher cracking activity than USY-zeolite-based catalysts, while the total acidity (Lewis and Bronsted acid

sites) of USY-zeolite-based catalysts higher than β-zeolite-based catalysts. This confirms that the catalytic cracking is not only dependent on the total acidity but also on the relative strength of acidic sites. Finally, they noted that the catalysts prepared by the physical mixing of zeolite with metal-loaded alumina show higher numbers of strong acid sites therefore consequently show higher cracking activity.

The aim of this work was to investigate the performance of ultra-stable-Y (USY) zeolite for hydrocracking of petroleum gas oil at reaction temperature of 450 $^{o}$C, 90 minutes contact time and 0.04 catalyst to gas oil ratio. The effect of different metals (NiMo, CoMo, NiW and CoW) loaded on USY zeolite on hydrocracking reaction was also studied. The catalysts characterizations using different techniques were presented and discussed.

## 2.0 Materials & Method

### *2.1 Materials*

Desulphurized petroleum gas oil (DS-GO) derived from sweet Far-East crude oil with density of 0.8260 kg/l at 15 $^{o}$C was used in this investigation. This sample was obtained from Shell Refinery Company Bhd., Port Dickson, Malaysia. The high purity gases nitrogen (99.999%) and hydrogen (99.999%) were obtained from Gas Pantai Timur Sdn. Bhd, Malaysia. A mixture of 5% $H_2S$ in $H_2$ balance was supplied by BOC, UK..

### *2.2 Catalyst*

Commercial USY zeolite with $SiO_2/Al_2O_3$ mole ratio of 5.5 was obtained from Tosoh USA Incorporation, USA in its $Na^+$ form. H-USY support was prepared by exchanging the sodium cation ($Na^+$) in its sodium form zeolite with ammonium ion ($NH_4^+$) in 4 M $NH_4Cl$ solution and shacked for 24 h. The formed product was consequently filtered and washed with distilled water until chloride free solution was obtained. The sample was kept to dry at 100 and $^{o}$C for 3 h then calcined at 500 $^{o}$C for 3 h. The chemical composition and physical properties of the USY zeolite provided by supplier are listed in Table 1. Synthesized NiMo, CoMo, NiW and CoW catalysts were prepared by impregnation of the USY zeolite with aqueous solution of metal precursor using the incipient wetness method. After impregnation the sample was dried at 110 $^{o}$C overnight, followed by calcinations at 500 $^{o}$C for 3 h in a muffle furnace [17,18]. The composition of the catalyst was 23% wt of $MoO_3$ (or $WO_3$) and 5.2% wt of NiO (or CoO). Prior to the reaction tests, the catalyst was pre-treated to increase its performance. About 2 g of the catalyst was placed in a stainless steel tubular reactor of 9 mm inside diameter and 130 mm length placed vertically inside tubular programmable temperature furnace. Nitrogen gas was introduced to the system to purge the air completely out of the system. During this purging operation the programmable temperature furnace was settled to give a heating rate of 10 $^{o}$C/min. when the temperature of the reactor reached the desired temperature (360 $^{o}$C), 5% $H_2S$ balance hydrogen gas was allowed to pass through the system at 40 $cm^3$/min for 3 h. On completion of the run, the furnace was switched off and the gas flow was turned off and allowing the nitrogen gas again to purge the system [19,20].

Table 1 Chemical composition and physical properties of the USY zeolite (Tosoh USA Incorporation, USA)

| Zeolite type | USY |
|---|---|
| Commodity | HSZ-320NAA |
| $SiO_2/Al_2O_3$ mole ratio | 5.5 |
| $Na_2O/Al_2O_3$ mole ratio | 1.00 |
| X-ray crystallinity, % | 101 |
| Physical state | Solid |
| Solubility | Insoluble in water |
| Appearance | White powder |

* Supplied by manufacture

### *2.3 The experimental set up*

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21cm inside diameter. The reactor was equipped with a vertical tubular furnace of 15 cm length and 5 cm diameter and used as heating source. This furnace was supplied by Watlow, USA, with maximum temperature of 1000 $^{o}$C. Type K thermocouples were placed outside and inside the reactor wall and were capable of monitoring temperature up to 1100 $^{o}$C. The schematic diagram of the experimental set up is shown in Fig. 1.

About 30 g of desulphurized petroleum gas oil (DS-GO) was firstly poured into the reactor, and then the catalyst was added in catalyst to gas oil ratio of 0.04. Hydrogen valve was opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor was then heated to reaction temperature of 450 $^{o}$C. The reaction was carried out for a fixed period of time 90 minutes after the reactor working temperature and pressure were attained.

The conversion, product yield, and catalyst to gas oil ratio were obtained using the following equations:

$$\% \text{ Conversion} = \frac{(W_{GO} - W_R)}{W_{GO}} \times 100 \quad (1)$$

where $W_{GO}$, $W_R$ are weight of gas oil and weight of unconverted fraction remained in the liquid product after distillation, respectively.

$$Y_I = \frac{W_I}{W_{GO}} \times 100 \quad (2)$$

where $Y_I$ is the yield of the product (wt%), I is the distillate fraction (gasoline, kerosene, diesel), $W_I$ is weight of the distillate fraction.

$$\text{Catalyst to gas oil ratio} = \frac{W_{CA}}{W_{GO}} \quad (3)$$

where $W_{CA}$ is weight of catalyst loaded.

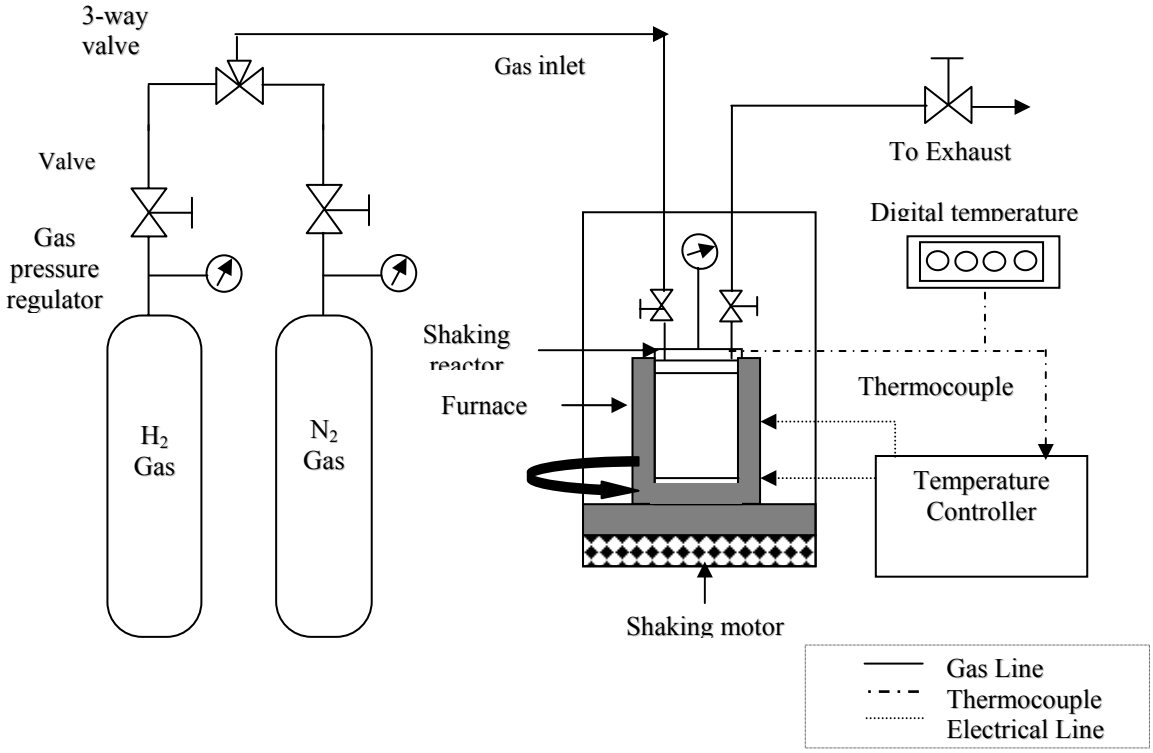


Figure 1 Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil

### *2.4 ASTM distillation analysis*

ASTM method D 86 was used to determine the product boiling range distribution and to investigate the yield of the lighter products after hydrocracking reaction. The distillation curve of the liquid products indicates the quantities of useful fractions to the refiner. The ASTM distillation unit was supplied by Hotech Instruments Corp. About 25 ml of product was poured into the distillation flask. The heater was started and the temperature at the neck of the distillation flask was recorder when the first drop of condensate was collected. The volume of condensate was taken down at the temperature 160, 200 and 240 $^{o}$C [21,22].

### *2.5 Gas Chromatograph (GC)*

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270cm-length × 3.15 mm stainless steel column (Supelco). The GC was equipped with flame ionization detector (FID). The flame ionization detector (FID) was used to find out the hydrocarbons components presented in gaseous product. The gases detected were hydrocarbons $C_1$-$C_5$. The identity of resulting GC peaks was defined by injecting standard gases to FID detector.

### *2.6. Characterization of catalysts*

#### *2.6. 1 Nitrogen Adsorption*

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300 $^{o}$C using Autosorb1 instrument before measurements were performed [23].

#### *2.6.2. Thermogravimetric Analyzer (TGA)*

Thermogravimetric analyzer (TGA) supplied by Perkin-Elemer, USA was used to study the thermal stability of the catalysts. About 5 mg of sample were loaded into a platinum pan and heated under nitrogen gas stream of 20 cm$^3$/min from ambient temperature to 900$^o$C with a control heating rate of 20$^o$C/min.

TGA-TPD (temperature–programmed desorption) was conducted on the same TGA instruments. About 5 mg of the sample was placed in a platinum pan and heated under nitrogen gas stream of 20 cm$^3$/min from ambient temperature to 500$^o$C with a control heating rate of 20$^o$C/min and hold at this temperature for 30 minutes. Then the temperature was lowered to 100$^o$C followed by injecting isopopylamine for 10 min. The desorption of physosorbed base molecules was allowed to continue at 100$^o$C for about one hour (until the mass nearly constant). The sample was heated to 700$^o$C at 20$^o$C/ min to desorb the chemisorbed isopropylamine. The chemisorption curve reveals the density and acid strength of the catalyst sample. The acidity was calculated by the following formula and reported in units of millimoles of acid sites per gram of catalyst:

$$Acidity = \frac{W\left(\frac{1}{Mb}\right)\left(\frac{1000mg}{1g}\right)}{Wz} \qquad (4)$$

where W is the mass loss due to the desorption of base in the temperature of interest (g), $W_Z$ is the mass of zeolite-based catalyst after pre-treatment (g), and Mb is the molecular weight of base (isopropyl amine).

TGA was also used to detect the percentages and type of coke deposited on catalysts after hydrocracking reactions. About 5 mg of coked catalyst were loaded into a platinum pan and heated under nitrogen gas stream of 20 cm$^3$/min from ambient temperature to 110$^o$C with a control heating rate of 20$^o$C/min. The nitrogen gas was replaced by the oxygen and temperature was increased to 800$^o$C.

## 3.0 Results and Discussion

### *3.1. Nitrogen adsorption measurements*

The BET surface areas, pore volumes and average pore diameters of support and catalysts are given in Table 2. It can be seen that the surface areas of catalysts are lower than that of support. This is reasonable as the impregnated metals both fill up and plug some of pores, making less area available for nitrogen adsorption, and contribute to the weight of the

catalyst, lowering the surface area measured on a weight basis. The pore volumes were estimated to be the liquid volume of nitrogen adsorbed at a relative pressure of 0.99. The pore volume of the support decreases after impregnated metals for the same reasons as the lower of the surface area.

Table 2 Characterization of USY and metal loaded USY.

| Catalyst | USY | NiMo/USY | CoMo/USY | NiW/USY | CoW/USY |
|---|---|---|---|---|---|
| Surface area, $m^2/g$ | 899 | 382 | 410 | 400 | 365 |
| Mesoporous area, % | 24.7 | 6.2 | 7.5 | 7.6 | 6.8 |
| Microporous area, % | 75.3 | 93.8 | 92.5 | 92.4 | 93.2 |
| Pore volume, $cm^3/g$ | 0.23 | 0.19 | 0.21 | 0.21 | 0.18 |
| Average pore size (APS), nm | 1.02 | 1.99 | 2.05 | 2.10 | 1.97 |
| Acidity, mmol $/g_{Cat}$ | 1.79 | 1.01 | 0.973 | 1.30 | 1.16 |
| Strong acidity, % | 46.7 | 45.9 | 72.5 | 49.9 | 46.4 |
| Weak acidity, % | 53.3 | 54.1 | 27.5 | 50.1 | 53.6 |

### *3.2. TGA-TPD acidity measurements*

The acid sites of commercial USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts were carried out using temperature programmed desorption (TPD). The TPD profiles of USY-based catalysts are shown in Fig. 2. The TPD measurements show that there are two acid sites in all USY-based catalysts, the peak in temperature range of 150-220$^o$C is associated to the weak acid site (Lewis type) and the second peak found in temperature range of 350-450$^o$C represents strong acid sites (Bronsted type). For commercial USY zeolite, two acid sites are found in temperature range of 150-220 and 280-380$^o$C. The number of Brønsted and Lewis acid sites is presents in Table 2. The total number of acid sites, measured by the amount of isopropylamine, was much more significant on all USY-based catalysts. Comparing the total acidity of the catalysts used in this study, one can conclude that the relative acidity of these catalysts is in the order:
USY > NiW/USY > CoW/USY > NiMo/USY > CoMo/USY

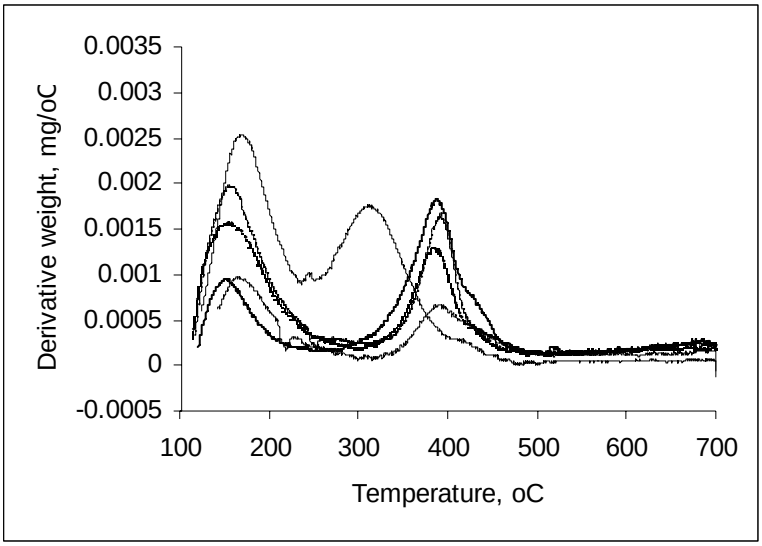


Figure 2 TGA-TPD acidity for different catalysts used in this study

### *3.3. Thermal stability analyzer (TGA)*

Thermal gravity experiments were carried out to study the stability of the catalysts. Fig. 3 shows the weight loss (TG) curves of five tested samples: USY zeolite and prepared NiMo/USY, NiW/USY, CoMo/USY and CoW/USY catalysts. It can be seen that two stages of thermal decomposition behaviour of the catalysts: a plateau from 30 to 120 $^{o}$C with a little weight loss due to the moisture release and a main weight of catalysts in the last stage. That means all catalysts showed high thermal stability in the temperature up to 700 $^{o}$C. This stability of the catalysts is favourable to prevent thermal decomposition of the catalysts during the reactions and regeneration process.

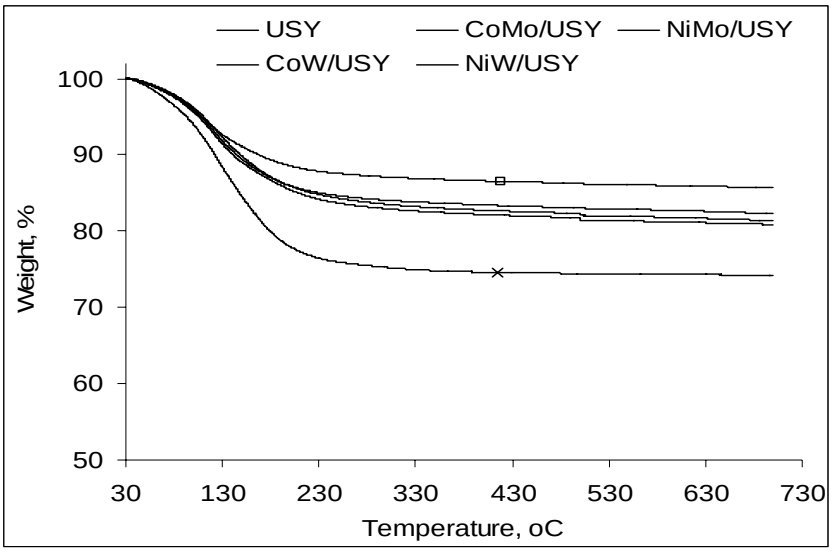


Figure 3 TGA thermal stability results for USY-based catalysts

### *3.4. Coke analysis*

Fig. 4 presents profiles of weight loss with temperature of coked USY, NiMo/USY, CoMo/USY, NiW/USY and CoW/USY catalysts. It can be seen that there are two general groups of coke formed in two temperature ranges, low range between 150-250 $^{o}$C (soft coke) and high range between 400-550 $^{o}$C (hard coke) for all catalysts used. The soft coke made up of oxygenated polyaromatic hydrocarbons below 250 $^{o}$C and accumulated on mesopores and external surface of the zeolite [24]. While, the hard coke built up of less oxygenated polyaromatic compounds at temperature range of 400-550 $^{o}$C and formed on Bronsted acid sites [25].

Oxidation of coke initiated from 150 $^{o}$C with steady decrease in weight until a sudden drop detected at 400-550 $^{o}$C. These temperatures reflected the ease or difficulty of the oxidation of coke and they were in the following order:
USY > NiW/USY > CoW/USY > NiMo/USY > CoMo/USY.

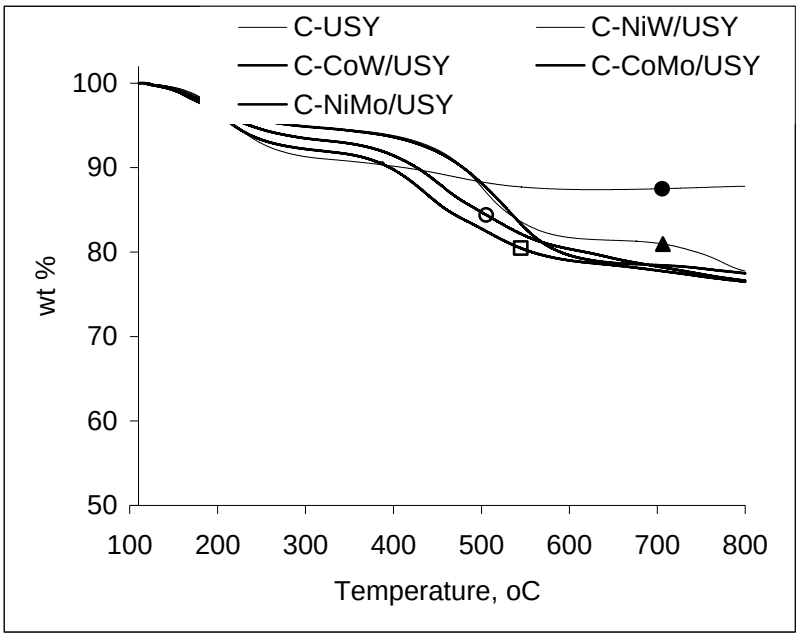


Figure 4 Profiles of weight loss with temperature of coked catalysts.

### *3.5. Product distributions*

The analyses of the gas oil are given in Tables 3 and 4. Hydrocracking of petroleum gas oil was studied at reaction temperature of 450 $^{o}$C, contact time of 90 minutes and catalyst to gas oil ratio of 0.04 using USY zeolite as support for NiMo, CoMo, NiW and CoW catalysts and their activity performance were investigated. The effect of catalysts types on the total conversion and products distribution obtained from hydrocracking of petroleum gas oil is shown in Table 5. Within experimental error, all the catalysts exhibited a very stable activity for the conversion of gas oil, and yielded the same reaction products, namely gasoline, kerosene, diesel, gas and coke, although NiW/USY catalyst may be somewhat favoured. It is interesting to compare the activities of USY-based catalysts with that of commercial USY zeolite. Over NiW-loaded catalyst, the conversion and total distillate fuels were 15.54 and 15.77 wt%, respectively higher than USY zeolite. There are two roles of NiW sulphide, one is the supply of hydrogen to acid sites, a supply of hydrogen is essential for continuous hydrocracking, and the other role is hydrogenation of aliphatic and aromatic compounds to paraffinic and cycloparaffinic compounds, respectively. Among the catalysts, NiW/USY catalyst showed more hydrocracking activity compared to other catalysts in terms of conversion and total distillate products. The hydrocracking activities of other USY-based catalysts were slightly increased as follows, from most active to least active: NiW/USY> NiMo/USY> CoW/USY > CoMo/USY > USY. Higher hydrocracking activity of NiW/USY catalyst is due to its relatively high surface area with higher pore size and higher acidity which favours successive cracking reactions, and as a consequence, the formation of light products. Therefore, the catalytic activity of NiW/USY catalyst is correlated to its higher acidity with 50 % strong acid sites (Bronsted acid sites). As known, to crack hydrocarbons, dual function catalysts, hydrogenation and cracking functions is needed. Supports provide the cracking functions, where the cracking takes place on acid sites.

The results show that the amount of both gas and coke obtained over all different types of the catalysts was around 8-12 wt% and the main gaseous products were hydrocarbons ethane, propane, $C_4^+$ and $C_5^+$.

Table 3 Distillation analysis of the gas oil

| Temperature, °C | Volume, % |
|---|---|
| 240 | IBP |
| 253 | 5 |
| 256 | 10 |
| 263 | 20 |
| 267 | 30 |
| 273 | 40 |
| 279 | 50 |
| 286 | 60 |
| 294 | 70 |
| 306 | 80 |
| 323 | 90 |
| 334 | 95 |
| 346 | FBP |

Table 4 Elemental composition analysis, wt % of the gas oil

| | |
|---|---|
| C | 85.17 |
| H | 14.74 |
| N | 0.087 |
| S | 0.003 |
| H/C atomic ratio | 2.077 |

Table 5 Product distribution of gas oil hydrocracking over USY-based catalysts.

| Catalyst | USY | NiMo/USY | CoMo/USY | NiW/USY | CoW/USY |
|---|---|---|---|---|---|
| Conversion (wt.%) | 47.81 | 58.41 | 52.21 | 63.35 | 53.69 |
| Total distilled fuels (wt.%) | 36.58 | 49.98 | 39.68 | 52.35 | 41.99 |
| Gasoline (wt.%) | 8.13 | 14.29 | 15.49 | 11.52 | 12.92 |
| Kerosene (wt.%) | 7.16 | 8.67 | 4.09 | 5.14 | 10.44 |
| Diesel (wt.%) | 21.29 | 18.63 | 20.10 | 35.69 | 18.63 |
| Gas yield (wt.%) | 5.13 | 3.67 | 6.73 | 5.23 | 5.73 |
| Gas composition (mol%) | | | | | |
| $CH_4$ | 0.01 | 0.02 | 0.01 | 0.01 | - |
| $C_2H_4$ | 0.23 | 0.15 | 0.19 | 0.28 | 0.20 |
| $C_2H_6$ | 38.98 | 39.45 | 37.35 | 42.42 | 41.19 |
| $C_3H_6$ | 1.88 | 1.13 | 1.62 | 1.91 | 1.56 |
| $C_3H_8$ | 31.50 | 32.68 | 31.27 | 29.15 | 30.32 |
| $C_4H_{10}$ | 19.51 | 19.65 | 20.53 | 18.35 | 18.43 |
| $C_5^=$ | 7.89 | 6.92 | 9.03 | 7.88 | 8.30 |
| Coke yield (wt.%) | 6.1 | 4.77 | 5.8 | 5.77 | 5.97 |

## 4.0 Conclusion

In this present work, petroleum gas oil was converted to distilled fuels (gasoline, kerosene and diesel) by catalytic hydrocracking over NiMo, CoMo, NiW and CoW catalysts supported on commercial USY zeolite at reaction temperature of 450 $^{o}$C, contact time of 90 minutes and catalyst to gas oil ratio of 0.04. A maximum value of liquid product (total distillate fuels) was obtained over NiW/USY catalyst, the values of total conversion and yield of total distillate fuels were 63.35 and 52.35 wt%, respectively, compared to 47.81 and 36.58 wt% over unloaded USY zeolite. The characterizations of catalysts were studied and product distributions over different catalysts were presented and discussed. NiW/USY catalyst possessed higher acidity with good balance between strong and weak acid sites. NiW/USY catalyst also showed very good thermal stability.

## Acknowledgement

The authors acknowledge the research grant provided by University Science Malaysia, Penang that has resulted in this article.

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